

A STUDY OF THE ACTIVITY OF FINELY DIVIDED METALS AND METALLIC OXIDES

DISSERTATION
SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES
OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
CLARENCE M. LOANE

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for the preparation of oxide catalysts whereby no impurity is introduced in large concentration and what foreign matter is present is easily removed. It is the purpose of this paper to develop in detail this new method for obtaining the oxides of nickel, cobalt, iron, manganese, and copper.

Two procedures were used for the preparation of the finely divided, pyrophoric metals: (1) Preparation of the metallic amalgams and subsequent removal of the mercury by distillation (4); (2) Reduction of the metallic salt by sodium in ammonia solution (5).

PREPARATION OF OXIDES OF METALS FROM AMALGAMS

The metallic amalgams were prepared by electrolysis of a slightly acid solution of the sulfates over a mercury cathode. The amalgams were vacuum distilled and the metal obtained in a pyrophoric condition. After oxygen had gradually come in contact with the metal so that at no time was a larger amount of heat generated, the product was tested for its catalytic efficiency.

Since the oxides prepared by the above method were not washed before testing, care was taken to purify the mercury and the sulfates used in the electrolysis.

The mercury was passed through a 6-foot nitric acid column four times and distilled three times.

Chemically pure sulfates were twice recrystallized. The electrolysis was carried out in a 400-cc. beaker. The concentration of the salt was chosen so that, by complete electrolysis of 300 cc. of solution, an approximately 2 per cent amalgam would be obtained. A few drops of sulfuric acid were added to the solution so prepared. Thirty cubic centimeters of mercury formed the cathode in the bottom of the beaker. The anode was of platinum gauze, except in the case of the manganese and iron salts. A current of approximately one ampere was used, so that the electrolysis was generally completed in twenty-four hours. Excess electrolyte was removed by washing the amalgam with distilled water.

In the case of the electrolytic preparation of the iron amalgam, an iron wire anode was used instead of the platinum gauze.

If the usual platinum anode was used when preparing the manganese amalgam, the amalgam was contaminated by scales of manganese dioxide forming at the anode and falling down on the amalgam. This difficulty was overcome by enclosing the anode in a glass tube, the bottom of which was formed by a porous clay disc. The inside of the tube was filled with concentrated ammonium nitrate solution. With these precautions observed, the electrolysis proceeded smoothly, without the formation of any dioxide. However, owing to the porous disc between the electrodes, only a small current could pass, and a week was necessary before a sufficiently concentrated amalgam was obtained.

In table 1 are listed the results of the above procedures.

Another method of obtaining the oxide catalysts was also used. The concentrated amalgam was exposed to the air until sufficient metal had separated as the oxide, and the powder was mechanically separated. Oxides of cobalt and of iron were readily obtained in this way. Nickel and manganese oxides were obtained in sufficient quantity only after several months. Copper amalgam was stable, no apparent oxidation taking place.

TABLE 1
Metallic oxides prepared from amalgams

METAL	NATURE OF AMALGAM	DISTILLATION TEMPERATURE	NATURE OF METAL	CONDITIONS OF OXIDATION	NATURE OF OXIDE
Nickel.....	Thick, smooth	degrees C. 190	Dull grey, fluffy mass	O ₂ stream 2 hours at 200°C.	Grey
Cobalt.....	Lumpy	250	Hard, grey, metallic lump	O ₂ stream 3 hours at 200°C.	Grey, metallic
Iron.....	Thick, lumpy	250	Hard, black lump	240°C. 3 hours	Dark red
Manganese.....	Smooth, dilute	200	Grey, porous lump	200°C. 18 hours	Dark brown
Copper.....	Thick, lustrous	200	Red, spongy	200°C. 10 hours	Surface—dark blue

PREPARATION OF OXIDES OF METALS OBTAINED BY REDUCTION IN
AMMONIA

Selected anhydrous salts of the metals were dissolved in ammonia and sodium added. The metals precipitated by the sodium were filtered, washed by ammonia, and allowed to oxidize slowly.

Anhydrous nitrates were used wherever possible. The nitrates cannot be dehydrated by heat treatment alone, for they decompose at a lower temperature than is necessary to drive off the water. A special method was necessary. That of Guntz and Martin (6) for the preparation of anhydrous cobalt and nickel nitrates seemed the most convenient. The nitrate was dissolved in its own water of crystallization at as low a temperature as possible and the solution poured into a large excess of fuming nitric acid. In several minutes the anhydrous salt precipitated. The

excess nitric acid was decanted, and the precipitate washed several times with fuming nitric acid. Most of the acid was decanted and the rest removed by vacuum distillation over quicklime and phosphorus pentoxide. This procedure was successfully applied to the nitrates of nickel, cobalt, and copper.

Ferric nitrate (nonahydrate) was partially dehydrated by a modification of the above method and was used in this imperfect state of dehydration.

Guntz also prepared anhydrous manganous nitrate by treating the hydrate with nitric anhydride. As this method is too involved to be practical, it was decided to prepare the iodide, even though the halides are generally undesirable in that they are poisons for the carbon monoxide oxidation. Manganous iodide, $\text{MnI}_2 \cdot 4\text{H}_2\text{O}$, was prepared by bubbling hydrogen iodide through a mixture of manganous carbonate and water. A concentrated solution of manganous iodide was thus prepared and, when dried in vacuum, it readily yielded the anhydrous iodide (7) as a pale brownish-pink solid.

TABLE 2

Oxides prepared by slow oxidation of metals obtained by reduction in ammonia

METAL	NATURE OF PRECIPITATE IN AMMONIA	TIME OXIDE WAS WASHED	FINAL PRODUCT
		<i>hours</i>	
Nickel.....	Brownish-black	24	Black
Cobalt.....	Very fine black	48	Black
Iron.....	Black	48	Red-brown
Manganese.....	Grey-brown	60	Grey-brown
Copper.....	Bronze	60	Brownish-black

An unsilvered 300-cc. Dewar flask was used as the reaction chamber. The use of such a vessel prevented the ammonia from evaporating rapidly and allowed the outer surface of the vessel to remain unfrosted so that the reaction could be observed.

The usual procedure for the reduction was as follows: the anhydrous salt was dissolved in ammonia, and sodium, freshly cut under petroleum ether, was added piece by piece as long as any reaction took place. This method was satisfactory for nickel, cobalt, manganese, and copper.

If the above routine was followed, the reduction of the incompletely dehydrated ferric nitrate was complicated by the formation of a complex and by the tendency of the added sodium to explode. In view of these difficulties, the roughly calculated amount of sodium was added first and the ferric nitrate later. The reduction then proceeded smoothly.

The precipitated metals were in all cases separated from the ammonia by suction filtering. The suction flask had to be immersed in an ether-dry ice mush to prevent the ammonia from boiling during the filtration. The

precipitate was washed on the filter by approximately one half liter of liquid ammonia. At no time was the precipitate sucked dry from ammonia; and, while the metal was still moist, it was removed from the filter and placed in a vessel such as an Erlenmeyer flask, into which air could enter only by diffusion. Although the metals all became hot enough to glow when the ammonia was removed rapidly (as was the case when the suction filtering was continued too long), the method of gradually admitting air as the ammonia slowly evaporated served as an efficient means of slow oxidation. Several hours usually suffice for the oxidation.

Manganese was so active that it became warm in the Erlenmeyer while still moist with ammonia. A cork placed loosely in the mouth of the flask cut down the supply of air sufficiently so that rapid oxidation ceased.

The metal oxides, along with sodium oxide, hydroxide, and amide as impurities, were then placed on the suction filter and washed with water. The purification was continued until the water in the suction flask failed

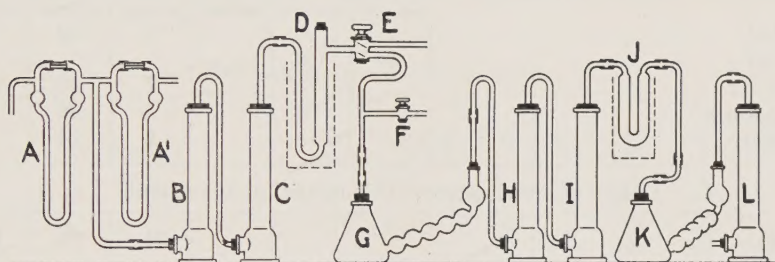


FIG. 1. CARBON MONOXIDE OXIDATION TRAIN

to give any test for sodium. The oxides (see table 2) were then dried and tested for catalytic effect.

The results of the above procedures are given in table 2.

METHOD OF TESTING CATALYTIC EFFICIENCIES

The apparatus for testing the efficiency of the catalyst is shown in figure 1. Two flowmeters, A and A', controlled the rate of the flow of carbon monoxide and oxygen. The valves of the carbon monoxide and oxygen storage tanks were adjusted to give a 1 per cent mixture of carbon monoxide in oxygen at a rate of 100 cc. per minute. The gases passed through a soda-lime tower, B, and a phosphorus pentoxide tower, C. The gaseous mixture then passed through the U-tube, D, which contained a 1 sq. cm. x 10 cm. bed of the catalyst. The carbon dioxide, formed during the passage over the catalyst, was absorbed in a solution of barium hydroxide contained in G. The residual gases were then swept through the soda-lime tower, H, and the phosphorus pentoxide tower, I. The dry mixture then passed through the U-tube, J, containing hopcalite main-

tained at 150°C. Any carbon monoxide which remained in the gas was completely oxidized by the hopcalite and was absorbed by the barium hydroxide in K. The remaining gas passed out through the soda-lime tower, L.

Stopcocks E and F were convenient for sweeping out the system and for regulating pressure when introducing barium hydroxide into the bubble tubes.

The catalysts obtained as hard lumps were broken up into smaller granules and sealed into the U-tube. Others of the oxides, in the form of

TABLE 3
Efficiencies of the catalysts expressed in per cent

TEMPERATURES	-78°C.	-40°C.	0°C.	30°C.	100°C.	150°C.
Oxides prepared by distillation of mercury and activation in oxygen						
Nickel.....				6	49	90
Cobalt.....	80	100				
Iron.....				7	50	100
Manganese*.....				5	38	62
Copper.....				2	24	
Oxides of metals prepared by reduction in ammonia						
Nickel.....				24	72	100
Cobalt†.....	100					
Iron.....					40	100
Manganese.....		0	100			
Copper.....				52	100	100

* Manganese and cobalt oxides, prepared by direct oxidation of the amalgam, were even more active, the latter being 100 per cent efficient at -78°C.

† The cobalt oxide was also tested before washing, when it contained at least 10 per cent impurity. Even with this large amount of sodium present, the oxide was 100 per cent efficient at 0°C. All the carbon dioxide formed by the oxidation was taken up by the sodium oxide, no carbon dioxide showing up in either bubble tube.

fine powder, were packed in the tube with pieces of broken glass so as to decrease the resistance to the gas stream. The tube containing the catalyst was placed in the train and heated to 150–200°C. while a current of oxygen passed through the system. This treatment, continued for several hours, served at once to dry the catalyst, to further the oxidation of any of the metal that had not been oxidized at room temperatures, and to remove any carbon dioxide from the train. Fifty cubic centimeters of a standard solution of barium hydroxide was introduced into each bubble tube, and the flow of the gases through the system started. After running

the test for the desired length of time, usually twenty minutes, the efficiency of the catalyst (see table 3) could be obtained by a determination of the amounts of barium hydroxide used up in the two bubble tubes. The percentage efficiency is the amount of barium hydroxide used up in the first bubble tube divided by the amount used in both bubble tubes. This was determined by titrating the unchanged barium hydroxide with standard acid.

COMPOSITION OF THE CATALYSTS

The catalysts from the amalgams were examined for mercury by precipitating with hydrogen sulfide. The cobalt and nickel catalysts showed the presence of a trace of mercury, but in the case of the other metals no mercury was found. It is unlikely that the small amount of mercury present would have any effect on the reaction.

In the case of the catalysts prepared by oxidation of metals precipitated in ammonia, sodium must have been present in small amounts. However,

TABLE 4
Comparison of activities of oxides

METALS	PRECIPITATED OXIDES (BENNETT)		OXIDES FROM AMALGAMS		OXIDES OF METALS FROM AMMONIA	
	At 30°C.	At 100°C.	At 30°C.	At 100°C.	At 30°C.	At 100°C.
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Nickel.....	100	100	6	49	24	72
Cobalt.....	100	100	100	100	100	100
Iron.....	0	1	7	50		40
Manganese.....	100	100	5	38	100	100
Copper.....	Reduction	100	2	24	52	100

alkalies have been shown to be poisons for this reaction (8) and could certainly have exerted no promoter action.

The amount of oxygen in the catalyst had no meaning. For example, analysis of one of the cobalt catalysts showed slightly less oxygen than corresponded to 2 oxygen:3 cobalt. In all cases the amount of oxygen varied according to the conditions of activation.

As is evident, it was not attempted to obtain a catalyst of definite composition, but it *was* shown here that the active metallic surface may be changed into an active oxide surface by a process of low temperature oxidation.

RELATIVE EFFICIENCIES OF OXIDIZED METALS AS CATALYSTS

Some idea of the activities of these oxides relative to those of precipitated oxides may be obtained from table 4.

As is evident from table 4, the method developed in this paper does not give oxides any more active than those precipitated and carefully purified. It does, however, offer another general method of preparing oxides whose activity is certainly comparable to that of those prepared by precipitation.

The percentage efficiencies given for the oxidized metals may be made to parallel those for the precipitated oxides even more closely if the following facts are taken into account.

The low results for nickel and manganese oxides from the amalgams are due to the insufficient oxidation of the metal. The oxides can be made more efficient by longer heating in oxygen.

Higher efficiencies may be expected in the case of nickel and manganese oxides (prepared by reduction in ammonia) if the washing is continued longer. The results given in table 4 are for the oxide washed for only one or two days. Longer purification slowly increased the efficiency.

The efficiencies of oxidized iron and copper are listed higher than those of the precipitated oxides. The results given in this work, however, are for a twenty minute run. At least part of the carbon monoxide oxidation below 100°C. involves chemical reduction of the oxides, for subsequent runs show decreasing efficiency of the catalyst.

The results obtained in this present work bring out an interesting point. It is the general belief that manganese dioxide is more active catalytically than the other oxides and that its presence as the essential oxide in commercial catalysts is uniquely responsible for the efficiency of those catalysts. The data presented here seemed to show that the oxide of cobalt is more active, or, at least, that it is less sensitive to impurities and generally easier to prepare in an active form.

SUMMARY

1. Methods have been developed for the low temperature oxidation of pyrophoric metals.

2. The oxidized metals have been tested as catalysts for the carbon monoxide oxidation. They have been found to be comparable in activity to the most carefully purified precipitated oxides.

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CARBONYL FORMATION OF THE PYROPHORIC METALS

It was attempted to prepare the metallic carbonyls by passing carbon monoxide over the pyrophoric metals that have been discussed previously. The carbonyl of the nickel from the amalgam was readily obtained in any desired amount. The cobalt from the amalgam yielded sufficient carbonyl for a distinct mirror test. None of these other attempts met with success, although, previously in this laboratory, Bennett had prepared the nickel and iron carbonyls by using the metals from the amalgams.

BIOGRAPHY

Clarence Morrison Loane was born in Baltimore, Md., on February 2, 1910. He received his elementary education in the public schools of this city and attended high school at the Baltimore City College. In 1926 he entered The Johns Hopkins University. He received the degree of Doctor of Philosophy in June, 1932.

